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(54) Polyolefin resin composition useful for packaging film

(57) A polyolefin resin composition useful for a packaging film which has a high heat shrinkage and an enhanced adhesion property and is effective for protecting a brittle cylindrical article, for example, a bottle, from breakage, comprises a polyolefin resin component (A) comprising at least one member selected from crystalline ethylene-propylene random copolymers and ethylene-propylene-other α-olefin terpolymers, an additional resin component (B) comprising at least one member selected from petroleum resins and hydrogenated petroleum resins, and a crystal nucleating agent (C) comprising at least one member selected from metal salts of organic carboxylic acids and magnesium silicate.

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POLYOLEFIN RESIN COMPOSITION USEFUL FOR PACKING FILM

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a polyolefin resin composition useful for packing film.

More particularly, the present invention relates to a polyolefin resin composition useful as a packaging film or labelling film having a high shrinkage in at least one direction and a close adhesion to articles to be packed and/or labelled, for example, cylindrical articles and bottles.

2. Description of the Related Art

It is known that polyolefin resin films produced by a biaxial drawing method have a high shrinkage in two directions and are useful for packing or wrapping various articles, for example, containers of instant foods such as instant Chinese noodles.

Also, it is known that, when bottles for whisky, fruit juice and other drinks are packed by using a high shrinkage plastic film, the bottles are prevented from breakage. This allows a reduction in the thickness of the bottle wall, resulting in a saving of material and energy for producing the bottles.

Further, when the surfaces of the packing or labelling films are printed with colors and patterns, the articles packed by the printed film exhibit an enhanced attractiveness and fashionability.

Conventional high shrinkage packing films are produced from a polyvinylchloride resin or polystyrene resin.

However, the conventional packing films consisting of the polyvinylchloride resin sometimes cause environmental pollution. Also, the conventional packing films made of the polystyrene resin are not satisfactory for protecting brittle articles, for example, bottles, from an impact force.

Accordingly, various attempts have been made to protect brittle articles such as bottles from an impact force by packing or wrapping the articles with a biaxially drawn polyolefin resin film having a high shrinkage in two directions. However, it was found that the conventional biaxially drawn polyolefin resin films are not adequate for packing the bottles.

Other attempts have been made to pack or wrap the bottles with a polyolefin resin packing film produced from a composition comprising at least one member selected from crystalline ethylene-propylene random copolymers and crystalline ethylene-propylene-other α-olefin terpolymers by a monoaxial drawing method and having a shrinkage in one direction.

However, these attempts were unsuccessful because the conventional monoaxially drawn polyolefin resin film had a relatively low heat shrinkage which made the shrinking temperature of the film undesirably high, and gave an unsatisfactory adhesion to the bottle surface, which adhesion decreased with a lapse of time.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a polyolefin resin composition useful as a packing film having a high shrinkage and a close adhesion.

Another object of the present invention is to provide a polyolefin resin composition useful as a heat-shrinkable packing film which is adequate for packing brittle articles, for example, bottles, at a relatively low temperature, and exhibits a close adhesion to the bottle surfaces over a long period without degradation.

The above-mentioned objects can be attained by the polyolefin resin composition of the present invention which comprises:

(A) 49.5% to 98.99% by weight of a polyolefin resin comprising at least one member selected from the group consisting of crystalline ethylene-propylene

random copolymers and crystalline ethylene-propylene-other α-olefin terpolymers;

(B) 1% to 50% by weight of an additional resin comprising at least one member selected from the group consisting of petroleum resins and hydrogenated petroleum resins; and

(C) 0.01% to 0.5% by weight of a crystal nucleating agent comprising at least one member selected from the group consisting of metal salts of organic carboxylic acids and magnesium silicate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the polyolefin resin composition of the present invention, the polyolefin resin component (A) is in an amount of from 49.5% to 98.99%, preferably from 70% to 95%, based on the total weight of the composition and comprises at least one member selected from crystalline ethylene-propylene random copolymers and crystalline ethylene-propylene-other α-olefin terpolymers.

A content of the polyolefin resin component (A) of less than 49.5% by meight results in undesirable breakage of the resultant film when it is stretched, unevenesss of the thickness of the film, and a decreased stability of the film-forming property.

Also, a content of the polyolefin resin component (A) of more than 98.99% results in an unsatisfactory shrinking property of the resultant film.

Preferably, the crystalline ethylene-propylene random copolymer has an ethylene content of 0.5% to 10% and a melt flow index (MFR) of 0.1 to 30 g/10 min determined in accordance with ASTM D1238, at a temperature of 230°C under a load of 2160 grams. Also, preferably, the crystalline ethylene-propylene-another α-olefin terpolymer has an ethylene content of 0.1% to 10% by weight, a propyl ne content of 80% to 99.8% by weight or more, a content of another α-olefin of 0.1% to 10% by weight, and a melt flow index of 0.1 to 30 g/10

min determined in accordance with ASTM D1238, at a temperature of 230°C under a load of 2160 grams.

The polyolefin resin component (A) may contain a minor amount, preferably 30% or less based on the weight of the polyolefin resin component (A), of an olefin rubber material, for example, ethylene-propylene rubber (EPR) or ethylene-propylene-diene terpolymer (EPDM), in addition to the crystalline ethylene-propylene random copolymer and/or the crystalline ethylene-propylene-other α-olefin terpolymer.

In the ethylene-propylene-other α-olefin terpolymer, the other α-olefin than propylene is preferably selected from butene-1, pentene-1. The most preferable other α-olefin is butene-1.

In the polyolefin resin composition of the present invention, the additional resin component (B) is in an amount of 1% to 50%, preferably 5% to 30%, based on the total amount of the composition and comprises at least one member selected from petroleum resins and hydrogenated petroleum resins.

If the content of the additional resin component (B) is less than 1% by weight, the resultant film exhibits an unsatisfactory heat-shrinking property.

If the content of the additional resin component (B) is more than 50% by weight, the resultant undrawn film becomes too adherent and sticky and thus, during the drawing procedure, the film often adheres to the cooling rolls and/or tenter clips. This phenomenon makes the drawing of the film difficult and thus, the quality of the resultant film is poor. Also, the resultant monoaxially drawn film exhibits an excessively large relaxation of the heat-shrinking stress and, therefore, is not adequate as a packing or wrapping file.

Usually, the petroleum resins and hydrogenated petroleum r sins preferably have a softening temperatur of 80°C to 150°C.

In the polyolefin resin composition of the present invention, the crystal nucleating agent is in an amount of 0.01% to 0.5%, preferably 0.01% to 0.3%, based on the total weight of the composition and comprises at least one member selected from metal salts of organic carboxylic acids and magnesium silicate.

If the crystal nucleating agent is used in an amount of less than 0.01%, the resultant packing film exhibits a decreased adhesion. Also, when the content of the crystal nucleating agent is more than 0.5% by weight, during the monoaxial drawing procedure, the resultant film is frequently broken and the drawn film exhibits a poor transparency.

The metal salts of organic carboxylic acids are preferably selected from alkali metal salts, alkaline earth metal salts, and aluminum salts of aromatic, aliphatic and cycloaliphatic carboxylic acids, for example, aluminum benzoate, sodium benzoate, barium benzoate. The most preferable metal salt is aluminum benzoate.

As the magnesium silicate, a talc is used which is produced by pulverizing natural hydrated magnesium silicate in the form of flakes or fibers.

Usually, the crystal nucleating agent is preferably in the form of fine particles having a size of 20 μm or less.

The polyolefin resin composition of the present invention may be mixed with an additive consisting of at least one member selected from, for example, antioxidants, antistatic agents, slip agents, anti-blocking agents, ultraviolet ray-absorbing agents, blowing agents, pigments, and inorganic fillers.

The polyolefin resin composition of the present invention is converted to a film by any conventional film-forming method.

Preferably, the polyolefin resin composition film

is produced by extruding a melt of the polyolefin resin composition through a film-forming die, cooling the resultant film-shaped stream of the polyolefin resin composition melt until solidified, and drawing the solidified, undrawn film in at least one direction.

When used for packing brittle cylindrical articles, for example, bottles, the film is in the form of a tube and the drawing procedure is carried out monoaxially in the transverse direction of the tube.

In the above-mentioned film-forming process, preferably, the extruding step is carried out at a temperature of from 180°C to 300°C, and the undrawn film has a thickness of 100 to 600 μm.

Also, the drawing step is preferably carried out at a draw ratio of 1.1 to 15.0. In the drawing step, preferably, the undrawn film is preheated at a temperature of 60°C to 200°C, is drawn at a temperature of 80°C to 200°C, and is heat set at a temperature of 40°C to 100°C.

The resultant monoaxially drawn film preferably has a thickness of from 30 to 120 μm and exhibits a heat shrinkage of 20% or more, preferably 30% or more, at a temperature of 100°C. The packing film can be used for packing at a temperature lower than 100°C.

When a brittle cylindrical article such as a bottle is packed by the monoaxially drawn polyolefin resin composition film of the present invention and is heated to thermally shrink the film, the shrunk film closely adheres to the surface of the article and protects the article from an impact force. For example, if the article is dropped, the shrunk film on the article prevents any breakage of the article.

The close adhesion property of the shrunk film does not change with a lapse of time and can be maintained at a satisfactory level for protecting the brittle articles from breakage thereof ov r a long period.

EXAMPLES

The present invention will be further explained by way of specific examples, which, however, are representative and do not restrict the scope of the present invention in any way.

In the examples, the heat-shrinkage and close adhesion of films were determined by the following methods.

1. Melt flow index (MFR) test

The melt flow index of a resin was determined in accordance with ASTM D1238, at a temperature of 230°C under a load of 2160 g.

2. Heat shrinkage test

A heat shrinkage of a film in a longitudinal or transverse direction was determined at a predetermined temperature, for example, 60, 80, and 100°C, in a glycerol bath in accordance with the following equation:

$$\text{Heat shrinkage (H.S. in \%)} = \frac{L_0 - L}{L_0} \times 100$$

wherein L_0 represents an original length of the unshrunk film L represents a length of the shrunk film.

3. Adhesion test

A monoaxially drawn film was shaped into a tube having a diameter monoaxial of 70 mm and a length of 133 mm. The drawing direction of the film becomes consistent with the circumference of the tube.

A bottle having a diameter of 68 mm and a height of 13.7 cm was packed by the tube-shaped film in such a manner that the monoaxial drawing direction of the film becomes consistent with the circumference of the bottle, and the upper end portion of the tube-shaped film extends over the shoulder of the bottle and the lower portion of the tube-shaped film extends over the bottom of the bottle.

The packed bottle was heated in a heating oven at a temperature of 220°C for 15 seconds to allow the tube-

shaped film to shrink and then closely adhere to the bottle surface, and then was left at room temperature for 30 to 60 minutes to stabilize the shrunk film.

The shoulder and bottom portions of the packed bottle were observed to determine whether the upper and lower portions of the shrunk film tube were closely adhered to these portions of the bottle.

After the stabilizing operation, when the upper and lower portions of the film tube were completely and entirely adhered to the shoulder and bottom portion of the bottle, the adhesion property of the film was represented by "good".

When at least a portion of the upper and lower portions of the film was separated from the shoulder and bottom portions of the bottle, the adhesion property of the film was represented by "bad".

Example 1

A polyolefin resin composition was prepared by admixing 85 parts by weight of a mixture of a crystalline ethylene-propylene random copolymer having a content of ethylene of 3.5% by weight and a melt flow index of 2.3 g/10 mg, and containing a small amount of a stabilizer and 2000 ppm of a crystal nucleating agent consisting of aluminum benzoate particle having an average size of 3.0 μm with 15 parts by weight of a hydrogenated petroleum resin (which was available under a trademark of Alcon P115 made by Arakawa Kagaku Kogyo K.K., and which had a melting point of 115°C) by a kneader, and was pelletized.

The pellets were converted to a thin film under the following conditions.

(1) Melt-extruding step

(a) Extruder: vent type extruder in which the second step portion is monoaxial.

(b) Temperature of resin: 230°C to 240°C

(c) Temperature of cooling roller: about 30°C

(d) V locity of take up roller: 7.5 m/min

(e) Extruding rate: 105 kg/hr

(2) Longitudinal monoaxial drawing step

(a) Draw ratio: 5.0

(b) Feed line velocity: 5 m/min

(c) Temperature of drawing roller: 70°C

(d) Heat-setting temperature: 50°C

(3) Transverse monoaxial drawing step

(a) Draw ratio: 5.0

(b) Feed line velocity: 5 m/min

(c) Temperature of drawing roller: 125°C

(d) Heat-setting temperature: 60°C

A portion of the resultant monoaxially drawn film was subjected to the heat shrinkage test, and another portion of the drawn film was subjected to the adhesion test.

The results are shown in Table 1.

Example 2

The same procedures as those described in Example 1 were carried out except that the polyolefin resin composition pellets were prepared from 75 parts by weight of a crystalline ethylene-propylene random copolymer having a content of ethylene of 3.5% by weight and a melt flow index of 2.3 g/10 min and containing a small amount of a stabilizer, and 3000 ppm of a crystal nucleating agent consisting of talc having an average size of 3 μm and 25 parts by weight of the same hydrogenated petroleum resin as described in Example 1.

The results are shown in Table 1.

Example 3

The same procedures as those described in Example 1 were carried out except that the polyolefin resin component consisted of a crystalline ethylene-propylene-butene-1 terpolymer having an ethylene content of 2% by weight, a propylene content of 98% by weight, a butene-1 content of 5% by weight and a melt flow index of 3.0 g/10 min.

The results are shown in Table 1.

Example 4

The same procedures as those described in Example 1 were carried out except that the hydrogenated petroleum resin was replaced by a petroleum resin (which was available under a trademark of ESCORE Z1315, was produced by EXXON CHEMICAL and had a softening point of 110°C to 120°C).

The results are shown in Table 1.

Comparative Example 1

The same procedures as those described in Example 1 were carried out except that the hydrogenated petroleum resin and the crystal nucleating agent were not used.

The results are indicated in Table 1.

Comparative Example 2

The same procedures as those described in Example 2 were carried out except that no crystal nucleating agent was used.

The results are shown in Table 1.

Comparative Example 3

The same procedures as those described in Example 1 were carried out except that the crystal nucleating agent consisted of benzoic acid.

The results are shown in Table 1.

Comparative Example 4

The same procedures as those described in Example 3 were carried out except that the crystal nucleating agent consisted of calcium carbonate particles.

The results are shown in Table 1.

Table 1

Item / Example No.		Drawing direction	Drawing temperature (°C)	Thickness of drawn film (μm)	Heat shrinkage (%) of drawn film 2 weeks after drawing				Adhesion property of film				General evaluation
									Immediately after drawing		After stabilizing		
					Shrinking direction	at 60°C	at 80°C	at 100°C	Shoulder of bottle	Bottom of bottle	Shoulder of bottle	Bottom of bottle	
Example	1	Longitudinal	70	40	MD(*)[1]	5	13	33	Good	Good	Good	Good	Good
		Transversal	125	40	TD(*)[2]	6	20	40	Good	Good	Good	Good	Good
	2	Longitudinal	70	40	MD	9	22	43	Good	Good	Good	Good	Good
		Transversal	125	40	TD	6	20	37	Good	Good	Good	Good	Good
	3	Longitudinal	70	40	MD	5	12	34	Good	Good	Good	Good	Good
		Transversal	125	40	TD	7	21	41	Good	Good	Good	Good	Good
	4	Longitudinal	70	40	MD	5	14	35	Good	Good	Good	Good	Good
		Transversal	125	40	TD	6	21	44	Good	Good	Good	Good	Good
Comparative Example	1	Longitudinal	70	40	MD	1	5	10	Bad	Bad	Bad	Bad	Bad
		Transversal	125	40	TD	1	6	12	Bad	Bad	Bad	Bad	Bad
	2	Longitudinal	70	40	MD	8	23	41	Good	Good	Bad	Bad	Bad
		Transversal	125	40	TD	6	22	40	Good	Good	Bad	Good	Bad

Table 1 (Continued)

Item / Example No.		Drawing direction	Drawing temperature (°C)	Thickness of drawn film (μm)	Heat shrinkage (%) of drawn film 2 weeks after drawing				Adhesion property of film				General evaluation
									Immediately after drawing		After stabilizing		
					Shrinking direction	at 60°C	at 80°C	at 100°C	Shoulder of bottle	Bottom of bottle	Shoulder of bottle	Bottom of bottle	
Comparative Example	3	Longitudinal	70	40	MD	7	28	38	Good	Good	Bad	Bad	Bad
		Transversal	125	40	TD	7	23	35	Good	Good	Bad	Bad	Bad
	4	Longitudinal	70	40	MD	8	13	40	Good	Good	Bad	Bad	Bad
		Transversal	125	40	TD	6	22	42	Good	Good	Bad	Bad	Bad

Note: $(*)^1$ --- Longitudinal

$(*)^2$ --- Transversal

CLAIMS

1. A polyolefin resin composition for packing film, comprising:

(A) 49.5% to 98.99% by weight of a polyolefin resin comprising at least one member selected from the group consisting of crystalline ethylene-propylene random copolymers and crystalline ethylene-propylene-other α-olefin terpolymers;

(B) 1% to 50% by weight of an additional resin comprising at least one member selected from the group consisting of petroleum resins and hydrogenated petroleum resins; and

(C) 0.01% to 0.5% by weight of a crystal nucleating agent comprising at least one member selected from the group consisting of metal salts of organic carboxylic acids and magnesium silicate.

2. The composition as claimed in claim 1, wherein the crystalline ethylene-propylene random copolymer has an ethylene content of 0.5% to 10% and a melt flow index (MFR) of 0.1 to 30 g/10 min determined in accordance with ASTM D1238, at a temperature of 230°C under a load of 2160 grams.

3. The composition as claimed in claim 1, wherein the crystalline ethylene-propylene-other α-olefin terpolymer has an ethylene content of 0.1% to 10% by weight, a propylene content of 80% to 99.8% by weight or more, a content of another α-olefin of 0.1% to 10% by weight, and a melt flow index of 0.1 to 30 g/10 min determined in accordance with ASTM D1238, at a temperature of 230°C under a load of 2160 grams.

4. The composition as claimed in claim 1, wherein the petroleum resin and hydrogenated petroleum resin have a softening temperature of from 80°C to 150°C.

5. The composition as claimed in claim 1, wherein the metal salts of organic acids are selected from the group consisting of aluminum benzoate, sodium benzoate

and barium benzoate.

6. The composition as claimed in claim 1, wherein the crystal nucleating agent is in the form of fine particles having a size of 20 μm or less.

7. A packing film comprising the polyolefin resin composition as claimed in claim 1.

8. The film as claimed in claim 7, which film has been produced by extruding a melt of the polyolefin resin composition through a film-forming die, by cooling the resultant film-shaped stream of the polyolefin resin composition melt to solidify same and by drawing the resultant undrawn film of the polyolefin resin composition in one direction.

9. The film as claimed in claim 7 which film has a thickness of 30 to 120 μm.

10. The film as claimed in claim 7, which film has a heat shrinkage of 20% or more at a temperature of 100°C.

11. A composition according to any of claims 1 to 6 in which the component A contains up to 30% by weight of an olefin rubber.

12. A composition according to any of claims 1 to 6 in which the other olefin in the terpolymer is butene-1 or pentene-1.

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